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(54) USE OF ALKOXYLATED COMPOUNDS AS NONIONIC EMULSIFIERS IN CROP PROTECTION FORMULATIONS

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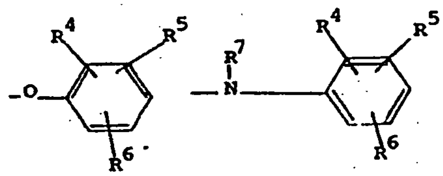
ABSTRACT OF THE DISCLOSURE: FEB 21 1984 1162409

The present invention relates to a crop protection formulation containing as a nonionic oil-in-water emulsifier a compound of the formula (I)

$$R^1\text{-}CH_2\text{-}\underset{\displaystyle OR}{\underset{|}{CH_3}}\text{-}CH_2\text{-}R^2 \qquad (I)$$

where R^1 and R^2 are identical or different and each is



, -O-α-naphthyl or -O-β-naphthyl, where R^4, R^5 and R^6 are identical or different and each is H, C_1-C_{12} -alkyl or C_7-C_{10} -aralkyl, R^3 is a radical of the formula (II) or (III)

$$-(C_2H_4O)_n(C_3H_6O)_mH \quad (II)$$

$$-(C_3H_6O)_m(C_2H_4O)_nH, \quad (III)$$

where n is a number from 0 to 50 and m is a number from 0 to 50, with the proviso that m or n is 5 or more, and R^7 is hydrogen.

USE OF ALKOXYLATED COMPOUNDS AS NONIONIC EMULSIFIERS IN CROP PROTECTION FORMULATIONS

Apart from a few exceptions, crop protection agents, such as insecticides, herbicides, fungicides and acaricides, are not applied to the crops to be protected as a 100 percent strength substance but in the form of ready-to-use diluted formulations. Amongst formulations which are very frequently used are emulsion concentrates, which, in addition to the water-insoluble active ingredient and a solvent, contain special emulsifiers or emulsifier mixtures which spontaneously emulsify the concentrate. An oil-in-water emulsion is then formed, i.e., the solvent, in which the active ingredient is dissolved, is in the form of small droplets constituting the disperse phase of the system. On the other hand, the active ingredient can also be dispersed directly in water, without a solvent, for which auxiliaries, in this case dispersing agents, are also required.

Numerous emulsifiers and dispersing agents for a variety of purposes are disclosed in the literature, for example, in German Published Application DAS 1,044,523, in which mixtures of alkylphenol oxyalkylates and of sulfonates of such phenol ethers are described as emulsifier systems for crop protection agents.

German Published Application DAS 2,053,356 discloses two-component emulsifier systems which come quite close to fulfilling the above requirements. These systems are mixtures of alkaline earth metal alkylarylsulfonates and

alkylphenols which have been oxyethylated and then oxypropylated.

This principle of using a mixture of nonionic and anionic surfactants is embodied in numerous other publications. Relatively small amounts of the mixture in most cases permit the spontaneous emulsification mentionied.

Several factors must be taken into consideration when selecting the nonionic component. It must first be ascertained whether the substance in question has sufficient emulsifying power for a wide range of crop protection agents and solutions thereof, and whether the ready-to-use diluted products are stable on storage, i.e., whether, during treatment of the crops, the liquors do not cream so that uniform distribution of the active ingredient becomes impossible.

Moreover, with crop protection agents which are generally sensitive and sometimes highly reactive substances, particular attention must be directed to possible chemical interactions between the emulsifier and the active ingredient. Otherwise the agent may become inactive or have a toxic effect on the crops themselves. Finally, the emulsifier itself must not be toxic to the crops to be treated.

In short, it can in no way be taken for granted that, for example, emulsifiers which are known for other industrial purposes and are capable of forming oil-in-water emulsions are also suitable emulsifying auxiliaries for crop protection formulations.

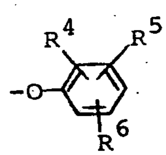
Purely inductive research in this field is not possible; satisfactory results can only be achieved empirically and demand time-consuming experiments and careful screening. It is also necessary to ensure that several emulsifier systems are available, since there is as yet no one system which fulfills all the above requirements.

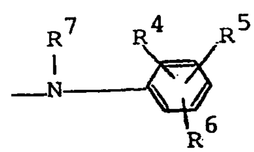
It would be advantageous to have non-ionic emulsifiers which, when used in small amounts, by themselves or as mixtures with anionic surfactants, provide optimum emulsification of a very wide range of crop protection agents, are tolerated by crops, inert towards the active ingredients, substantially non-toxic, and give ready-to-use emulsions or dispersions which are stable for 6 hours or more.

The present invention, in general relates to compounds of the formula (I).

$$R^1-CH_2-\underset{\displaystyle OR^3}{\underset{|}{CH}}-CH_2-R^2 \qquad (I)$$

where R^1 and R^2 are identical or different and are





, -O-α-naphthyl or

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-O-β-naphthyl, where R^4, R^5 and R^6 are identical or different and each is H, C_1-C_{12}-alkyl or C_7-C_{10}-aralkyl, R^3 is a radical of the formula (II) or (III)

$$-(C_2H_4O)_n(C_3H_6O)_mH \qquad \text{(II)}$$

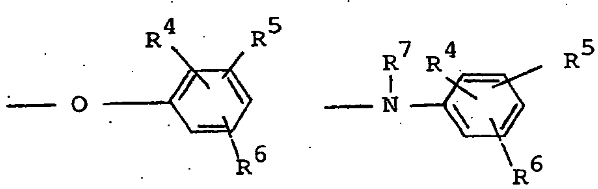
$$-(C_3H_6O)_m(C_2H_4O)_nH, \qquad \text{(III)}$$

where n is a number from 0 to 50 and m is a number from 0 to 50 with the proviso that m or n is 5 or more, and where R^7 is hydrogen.

The present invention in particular provides a crop protection composition comprising a crop protecting agent and as a nonionic oil-in-water emulsifier an effective amount of a compound of the formula (I)

$$R^1\text{-}CH_2\text{-}\underset{\displaystyle |\atop \displaystyle OR^3}{CH}\text{-}CH_2\text{-}R^2 \qquad \text{(I)}$$

where R^1 and R^2 are identical or different and each is



,-O-α-naphthyl or -O-β-naphthyl, where R^4, R^5 and R^6 are identical or different and each is H, C_1-C_{12}-alkyl or C_7-C_{10}-aralkyl , R^3 is a radical of the formula (II) or (III)

$$-(C_2H_4O)_n(C_3H_6O)_mH \qquad \text{(II)}$$

$$-(C_3H_6O)_m(C_2H_4O)_nH, \qquad \text{(III)}$$

where n, is a number from 0 to 50 and m is a number from 0 to 50 with the proviso that m or n is 5 or more, and R^7 is hydrogen, said composition, if desired, including a suitable solvent for said agent or water and a suitable solvent for said agent.

In accordance with the present invention there is provided a crop protection formulation suitable for the preparation of a crop protection oil-in-water emulsion, said formulation compris-

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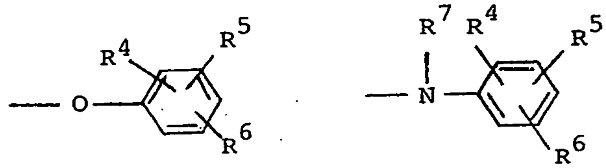
ing a crop protecting agent and as a nonionic oil-in-water emulsifier an effective amount of a compound of the formula (I)

$$R^1\text{-}CH_2\text{-}\underset{\displaystyle OR^3}{\underset{|}{CH}}\text{-}CH_2\text{-}R^2 \qquad (I)$$

where R^1 and R^2 are identical or different and each is



,-O-α-naphthyl or -O-β-naphthyl, where R^4, R^5 and R^6 are identical or different and each is H, C_1-C_{12}-alkyl or C_7-C_{10}-aralkyl, R^3 is a radical of the formula (II) or (III)

$$-(C_2H_4O)_n(C_3H_6O)_mH \qquad (II)$$

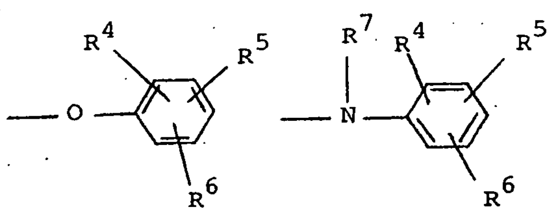
$$-(C_3H_6O)_m(C_2H_4O)_nH \qquad (III)$$

where n is a number from 0 to 50 and m is a number from 0 to 50, with the proviso that m or n is 5 or more, and R^7 is hydrogen, said formulation, is desired, including a suitable solvent for said agent.

The present invention additionally provides a crop protection oil-in-water emulsion comprising 1) a crop protecting agent, 2) as a nonionic oil-in-water emulsifier an effective amount of a compound of the formula (I)

$$R^1\text{-}CH_2\text{-}\underset{\displaystyle OR^3}{\underset{|}{CH}}\text{-}CH_2\text{-}R^2 \qquad (I)$$

where R^1 and R^2 are identical or different and each is



, -O-α-naphthyl or

-O-β-naphthyl, where R^4, R^5 and R^6 are identical or different and each is H, C_1-C_{12}-alkyl or C_7-C_{10}-aralkyl, R^3 is a radical of the formula (II) or (III)

$$-(C_2H_4O)_n(C_3H_6O)_mH \qquad (II)$$

$$-(C_3H_6O)_m(C_2H_4O)_nH, \qquad (III)$$

where n is a number from 0 to 50 and m is a number from 0 to 50, with the proviso that m or n is 5 or more, and R^7 is hydrogen, 3) a suitable solvent for said agent and 4) water.

Compounds of the formula (I), where R^1 and R^2 are the phenoxy or naphthoxy radicals defined, are already known as emulsifiers from German Laid-Open Application DOS 2,839,463. However, their possible use as an emulsifier component in crop protection formulations was not obvious since the publication mentioned discloses these surfactants only as examples of emulsifiers or disersing agents in printing pastes, which, as is known, contain thickeners which give the paste the high viscosity it needs. The litterature reference contains no indication of the fact that mobile emulsions which are stable for more than 6 hours, such as the emulsions required for applying crop protection agents, for example, by means of spraying machinery, can also be obtained.

Moreover, the above publication also contains no indication of the agents also being used together with

anionic components (such a measure is even harmful in the case of printing pastes) and, finally, it also states that anti-foam agents are used, from which it may be concluded that the emulsifiers foam too much, or are not by themselves capable of suppressing foaming. Severe foaming, however, greatly impedes proper application of active ingredient emulsions. No foaming was observed during the use according to the invention.

Finally, it was also not be be expected that, as already mentioned, this class of substances would be suitable for crop protection agent concentrates in the same way as the pure alkylphenol oxyalkylates of German Published Application DAS 2,053,356, since it could not be expected without reservations that these non-ionic emulsifiers derived from aliphatic alcohol derivatives would have the same properties with respect to tolerance by crops and compatibility with the active ingredients.

The nonionic emulsifiers to be used according to the invention are prepared in a simple manner, for example by first treating a phenol or naphthol or a mononuclear aromatic amine (substituted or unsubstituted aniline) with an alkali metal hydroxide and then reacting the mixture with epichlorohydrin. The resulting 1,3-disubstituted glycerol ether or 1,3-diaminoalcohol is then oxyalkylated with ethylene oxide by itself and, if desired, subsequently with propylene oxide, or vice versa.

These reaction steps are known and do not require further explanation; for better understanding, the relevant preparation examples may be referred to.

The emulsifiers can be used, in the formulations, either by themselves or, preferably, as mixtures with anionic surfactants, especially the alkaline earth metal salts, preferably the calcium salts, or mono- or di-alkylbenzene-sulfonates, where alkyl is of 8 to 12 carbon atoms. The weight ratio of nonionic compound to anionic surfactant in the mixture should preferably be from 75:25 to 30:70, but not less than 30 percent by weight based on the mixture of the nonionic component should be present.

The crop protection agents may be converted into formulations by adding from 2 percent to 15 percent by weight, preferably from 3 percent to 8 percent by weight, of the emulsifier system according to the invention to the crop protection agent, which is either neat or in the form of a 10 percent to 90 percent strength by weight, preferably 40 percent to 85 percent strength by weight, solution in an organic inert solvent having a boiling point from 80°C to 200°C, preferably a xylene, toluene or another aromatic or aliphatic solvent (e.g., a gasoline fraction) conventionally employed for formulating crop protection agents. The emulsifier system can be undiluted or in the form of a 20 percent to 85 percent strength solution in a polar solvent, such as an alcohol of 3 to 8 carbon atoms, dimethylformamide or N-methylpyrrolidone.

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The resulting emulsion concentrate of the crop protection agent can easily be diluted with water to give a ready-to-use liquor which can be kept for more than 6 hours and displays no creaming or sedimenting even in hard water. It is possible to prepare, for example, emulsions of as low as 0.1 percent strength. In general, emulsions containing from 0.2 to 2 percent by weight of active ingredient are prepared. Examples of nonionic emulsifiers which can be used are given in Table 1 which follows:

Table 1

Compounds of the formula I

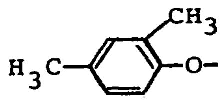
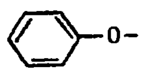
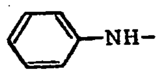
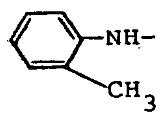
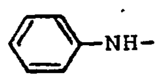
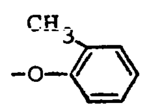
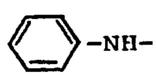
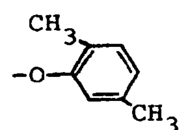
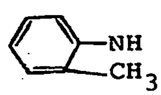
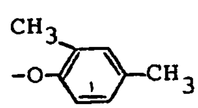
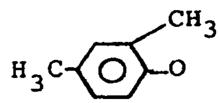
No.	R^1	R^2	n	m
1		$R^2=R^1$	0	0
2	"	"	2.0	0
3	"	"	5.5	0
4	"	"	8.0	0
5	"	"	10.0	0
6	"	"	12.0	0
7	"	"	16.0	0
8	"	"	18.0	0
9	"	"	19.5	0
10	"	"	22.0	0
11	"	"	23.0	0
12	"	"	27.0	0
13	"	"	32.5	0
14		"	18.0	0
15		"	17.5	0
16		"	17.0	0
17			18.5	0
18			17.0	0
19		CH_3 (sic) -O- (sic)	17.0	0
20	$H_{37}C_{18}$-NH-		21.5	0

Table 1
(continued)

No.	R^1	R^2	n	m
21		$R^2=R^1$	0	15
22	"	"	0	5
23	"	"	18	4.5
24	"	"	18	5

Examples 1-20 which follow describe the synthesis of the substances listed in Table 1.

Example 1

In a reaction vessel 610 parts (5 molar units) of 2,4-dimethylphenol and 300 ml of dioxane are heated to 30°C to 50°C, with stirring, and 110 parts (2.75 molar units) of sodium hydroxide powder are added at this temperature. The mixture is then heated to 90°C to 95°C and is stirred at this temperature for 2 hours. Then 231 parts (2.5 molar units) of epichlorohydrin are allowed to run in over 30 minutes and the mixture is subsequently reluxed for 4 hours. The sodium chloride precipitated is filtered off, and the dioxane is distilled from the filtrate under reduced pressure. Obtained are 688 parts by weight of 1,3-bis(2,4-dimethylphenyl)glycerol ether.

Example 2

In a reaction vessel 2 parts of potassium hydroxide are added to 300 parts (1 molar unit) of 1,3-bis-(2,4-dimethylphenyl)glycerol ether and the mixture is reacted with 88 parts (2 molar units) of ethylene oxide, which is added a little at a time, at from 110°C to 120°C in a stirred autoclave. The pressure is from 4 bars to 9 bars. Obtained are 386 parts of a pale yellow pasty substance.

Examples 3-13

The above bisphenyl-glycerol ether is reacted with ethylene oxide by the procedure described in Example 2. The degree of ethoxylation is given in Table 2. This number indicates that 1 mole of the hydroxyl-containing 1,3-bisaryl-glycerol ether is reacted with n times the molar amount of ethylene oxide.

Table 2

No.	ETHYLENE OXIDE Moles	Parts
3	5.5	242
4	8.0	352
5	10.0	440
6	12.0	528
7	16.0	704
8	18.0	792
9	19.5	968
10	22.0	968
11	23.0	1,012
12	27.0	1,188
13	32.5	1,430

Example 14

In a reaction vessel 470 parts of phenol are reacted with 321 parts of epichlorohydrin to give 562 parts of 1,3-bisphenyl-glycerol ether by a method similar to that of Example 1. The ether is reacted with 18 moles of ethylene oxide by a method corresponding to that of Example 2.

Example 15

In a reaction vessel 66 parts (1.65 molar units) of sodium hydroxide powder are added to 465 parts (5.0 molar units) of aniline, with stirring. The mixture is heated to

90°C. At this temperature 139 parts (1.5 molar units) of epichlorohydrin are slowly added during the course of 30 minutes and the mixture is then refluxed for 7 hours. It is then allowed to cool. The sodium chloride precipitated is separated off and the excess aniline is distilled off. Remaining in the form of a viscous liquid are 352 parts of 1,3-dianilinopropan-2-ol.

Then 1.2 parts of potassium hydroxide are added to 121 parts (0.5 molar units) of the 1,3-dianilinopropan-2-ol and the mixture is reacted with 390 parts (8.75 molar units) of ethylene oxide, which is forced in a little at a time, at from 110°C to 125°C in a stirred autoclave. The pressure is from 3 bars to 9 bars. Obtained are 515 parts of a yellowish viscous liquid.

Example 16

In a reaction vessel 1,070 parts (10 molar units) of N-methylaniline are heated to 70°C, and 925 parts (10 molar units) of epichlorohydrin are added dropwise at this temperature in the course of 90 minutes. The reaction mixture is then heated to 80°C and is stirred at this temperature for 3.5 hours. It is subsequently allowed to cool to room temperature and 880 parts (11.0 molar units) of 50 percent strength sodium hydroxide solution are added dropwise at 20°C in the course of 45 minutes. This mixture is stirred overnight at room temperature, and, after the sodium chloride formed and the water have been separated, 1,596 parts of N-methylanilinoglycidylamine are obtained as a light yellow liquid of epoxide content 95 percent.

Then 1,585 parts (9.7 molar units) of N-methylanilinoglycidylamine are mixed with 2,082 parts (19.5 molar units) of N-methylaniline and 62 parts of sodium methylate and the mixture is heated to 200°C under a nitrogen atomsphere with stirring. The mixture is refluxed for 6 hours and the excess N-methylaniline is then distilled off. Obtained is 1,3-di-(N-methylanilino)-propan-2-ol as a light brown solid substance of melting point 78°C to 80°C.

Then 0.9 part of potassium hydroxide is added to 94.5 parts (0.35 molar units) of 1,3-di-(N-methylanilino)-propan-2-ol and the mixture is reacted with 264 parts (6 molar units) of ethylene oxide, which is added a little at a time, at from 120°C to 125°C in a stirred autoclave. The pressure is from 4 bars to 8 bars. Obtained are 358 parts of a yellowish water-soluble solid substance.

Example 17

In a reaction vessel 186 parts (2 molar units) of aniline are heated to 80°C and 185 parts (2 molar units) of epichlorohydrin are added dropwise in the course of 50 minutes. The mixture is subsequently stirred at 195°C for 4 hours; first 244 parts (2 molar units) of 2,4-dimethylphenol and then 176 parts of 50 percent strength sodium hydroxide solution (2.2 molar units) are added at 80°C and the mixture is heated at 110°C for 8 hours. It is then cooled and 250 parts of water are added. Stirring is continued for one-half hour and the phases are then separated in a separating funnel. Residual water is removed in

a rotary evaporator at 80°C/20 mm Hg. Finally, the residue is reacted with 1,628 parts of ethylene oxide at 120°C in an autoclave by a method similar to that in Example 2. Obtained are 2,144 parts of a yellow pasty substance.

Example 18

In a reaction vessel 186 parts of aniline are reacted with 185 parts of epichlorohydrin and 244 parts of 2,5-dimethylphenol by a method similar to that of Example 17. Obtained are 525 parts of a glycerol ether-amine which is oxyethylated with 1,496 parts of ethylene oxide by a method corresponding to that in Example 2. Obtained are 2,116 parts of a yellow pasty substance.

Example 19

In a reaction vessel 214 parts (2.0 molar units) of N-methylaniline are heated to 75°C. Then 185 parts (2.0 molar units) of epichlorohydrin are added dropwise in the course of 30 minutes, with stirring, and stirring is continued for an additional 4.5 hours at 90°C to 95°C.

The mixture is then allowed to cool to 50°C and 244 parts (2.0 molar units) of 2,5-dimethylphenol are added a little at a time. Then 176 parts of 50 percent strength sodium hydroxide solution (2.2 molar units) are added dropwise in the course of 15 to 20 minutes. The reaction mixture is subsequently heated to 110°C and is stirred at this temperature for 8 hours.

The mixture is then allowed to cool to 50°C and the sodium chloride formed is removed by washing with 250

parts by volume of water. After the water has been separated off, 565 parts of a brownish viscous liquid are obtained.

Then 1 part of potassium hydroxide is added to 114 parts (0.4 molar unit) of this liquid and the mixture is reacted with 299 parts (6.8 molar units) of ethylene oxide at from 120°C to 125°C and under a pressure of from 4 bar to 9 bars in a stirred autoclave. Obtained are 411 parts of a water-soluble viscous substance.

Example 20

In a reaction vessel 269 parts (1 molar unit) of stearylamine are heated at 80°C and 92.5 parts (1 molar unit) of epichlorohydrin are added dropwise to the clear melt in the course of 35 minutes. The mixture is subsequently stirred at 95°C for 4.5 hours. Then 122 parts (1 molar unit) of 2,4-dimethylphenol are added at 80°C, and 88 parts of 50 percent strength sodium hydroxide solution (2.2 molar units) are added at 60°C. The mixture is heated to 110°C for 8 hours and is then allowed to cool. Then 250 parts of water are added and stirring is continued for one-half hour. The phases are then separated and residual water is stripped from the organic phase under reduced pressure. Obtained are 423 parts of a brown viscous liquid which is reacted with 946 parts of ethylene oxide in an autoclave by a method similar to that in Example 2. Obtained are 1,361 parts of a yellow pasty substance.

The substances listed and described above have the general formula

$$\begin{array}{l} R^1-CH_2-\underset{|}{C}H-CH_2-R^2 \\ \qquad\quad O-(CH_2-CH_2-O)_n-(CH-\underset{\displaystyle CH_3}{\underset{|}{C}}H_2-O)_m-H \end{array}$$

or

$$\begin{array}{l} R^1-CH_2-\underset{|}{C}H-CH_2-R^2 \\ \qquad\quad O-(\underset{\displaystyle CH_3}{\underset{|}{C}}H-CH_2-O)_m-(CH_2-CH_2-O)-H \end{array}$$

are particularly suitable as nonionic emulsifiers for the purposes of the invention.

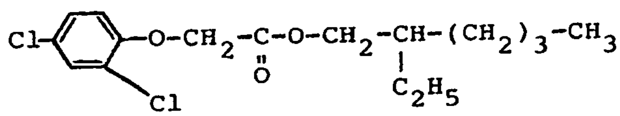
The marked crystallization-delaying effect of the novel surfactants is found to be an advantage, especially in the case of emulsion concentrate formulations of solid active ingredients which have an extremely strong tendency to crystallize in the emulsions.

Compared with the conventional non-ionic emulsifiers described in the publications referred to at the outset, the above substances have equally good, and in some cases better, emulsifying properties.

Examples 21-27, which follow, describe the preparation of various crop protection formulations which incorporate the emulsifiers described in Examples 1-20.

Example 21

The herbicidal active ingredient isooctyl-2,4-dichlorophenoxyacetate

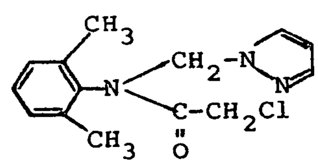


was formulated as an emulsion concentrate, containing 47.0 percent of active ingredient, 0.8 to 2.4 percent of calcium dodecylbenzenesulfonte, 1.6 to 3.2 percent of substances from Examples 4, 6, 7-19, 23 and 24, and petroleum to 100.0 percent.

A 0.2 percent strength emulsion and a 2.0 percent strength emulsion exhibited excellent stability when tested at room temperature over a period of 6 hours.

Example 22
(Comparison)

A herbicidal active ingredient having the following formula



was formulated as an emulsion concentrate containing 20 percent of active ingredient, 5 percent of calcium dodecylbenzenesulfonate, 5 percent of castor oil ethoxylated with 48 moles of ethylene oxide, and xylene to 100 percent.

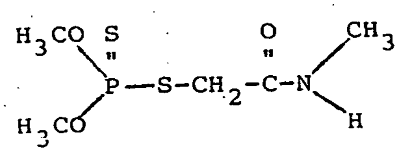
Extremely large quantities of crystals were formed in a 0.2 percent strength emulsion, and were also formed in a 2.0 percent strength emulsion after 1 to 2 hours at room temperature or 1/2 hour at 10°C.

When the same concentration of 5 percent of the substance of Example 8 from Table 1 was used instead of the oxyethylated castor oil, no crystals formed even after 10 hours at 10°C.

An equally stable emulsion was also obtained when the substances of Example 4-7, 9-16, 16, 20 and 24 were used in amounts of from 1 to 8 percent, depending on the degree of oxyethylation.

Example 23

An insecticidal active ingredient dimethoate (as the commercial product Perfekthion*) of the following formula



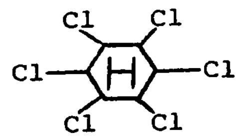
was formulated as an emulsion concentrate containing 40 percent of active ingredient, 5 percent of cyclohexanone, 8 percent of the substances of Examples 5, 7-20 and 22-24, and xylene to 100 percent.

The amount of substance according to the invention is constant at 8 percent and does not depend on the degree of oxyethylation. The emulsions (0.2 percent strength and 2.0 percent strength) remain stable for a period of 6 hours.

* Trade mark

Example 24

Another insecticidal active ingredient, Lindane®, (as the commercial product Perfekthion Fluid) of the following formula

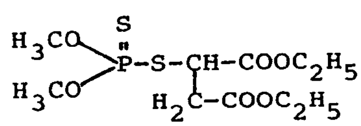


was formulated as an emulsion concentrate containing 20 percent of active ingredient, 1 to 3 percent of calcium dodecylbenzenesulfonate, 1 to 3 percent of the substances of Examples 7, 10, 12, 13 and 24, and xylene to 100 percent.

The stability of the emulsion is satisfactory over a period of 6 hours.

Example 25

Malathion®, which is also an insecticidal active ingredient, of the following formula

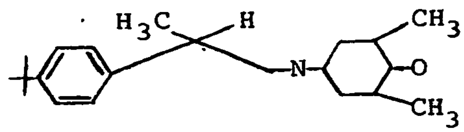


was formulated as an emulsion concentrate containing 40 percent of active ingredient, 1 to 2 percent of calcium dodecylbenzenesulfonate, 1 to 2 percent of the substances of Examples 5-7, 16, 19, 23 and 24, and xylene to 100 percent.

The emulsions have satisfactory stability.

Example 26

The following substance was used as a fungicidal active ingredient:



(cis-form)

The emulsion concentrate had the following composition: 50 percent of active ingredient, 2 to 6 percent of calcium dodecylbenzenesulfonate, 4 to 8 percent of the substances of Examples 4-13, 23 and 24, and cyclohexanone to 100 percent.

Example 27

Sulfur suspension concentrates (p = 1.45 g/cm^3) of the following formulations were prepared using the substances listed in Table 1, the particle size of the sulfur being brought to $\geqslant$ 90 percent $<2\ \mu$ by appropriate physical methods: 55 percent of sulfur, 5 percent of antifreeze, 3.5 percent of dispersant, 2 percent of oxyethylated nonylphenol, 2 percent of inert material, 2 percent of one of the above substances of Example 5 and 7-19, and water to 100 percent.

Prepared were 0.2 percent strength and 2.0 percent strength suspensions.

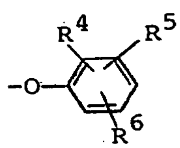
The stabilities of these suspensions were satisfactory, for all samples, over a period of 6 hours at room temperature.

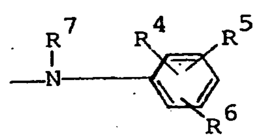
The embodiments of the invention in which an exclusive privilege or property is claimed are defined as follows:

1. A crop protection formulation suitable for the preparation of a crop protection oil-in-water emulsion, said formulation comprising a crop protecting agent and as a nonionic oil-in-water emulsifier an effective amount of a compound of the formula (I)

$$R^1\text{-}CH_2\text{-}\underset{\displaystyle OR^3}{\underset{|}{CH}}\text{-}CH_2\text{-}R^2 \qquad (I)$$

where R^1 and R^2 are identical or different and each is





, -O-α-naphthyl or -O-β-naphthyl, where R^4, R^5 and R^6 are identical or different and each is H, C_1-C_{12}-alkyl or C_7-C_{10}-aralkyl, R^3 is a radical of the formula (II) or (III)

$$-(C_2H_4O)_n(C_3H_6O)_mH \quad (II)$$

$$-(C_3H_6O)_m(C_2H_4O)_nH, \quad (III)$$

where n is a number from 0 to 50 and m is a number from 0 to 50, with the proviso that m or n is 5 or more, and R^7 is hydrogen , said formulation, if desired, including a suitable solvent for said agent.

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2. The crop protection formulation of claim 1 wherein the amount of the nonionic emulsifier is from 2 percent to 15 percent by weight, based on the weight of the crop protection agent.

3. The crop protection formulation of claim 2 wherein an anionic surfactant is used in addition to the nonionic emulsifier.

4. The crop protection formulation of claim 3 wherein the anionic surfactant is a calcium salt of a mono- or dialkylbenzene sulfonate.

5. The crop protection formulation of claim 4 wherein the weight ratio of nonionic surfactant to anionic surfactant is from 75:25 to 30:70.

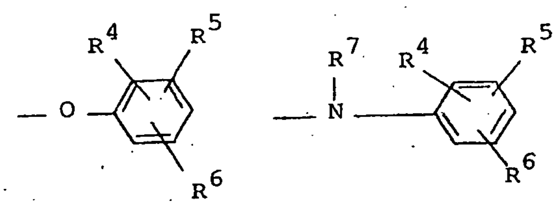
6. The crop protection formulation of claim 5 which contains xylene or toluene as a solvent.

7. The crop protection formulation of claim 1 wherein the amount of nonionic emulsifier is from 3 percent to 8 percent by weight based on the weight of the crop protection agent.

8. A crop protection oil-in-water emulsion comprising 1) a crop protecting agent , 2) as a nonionic oil-in-water emulsifier an effective amount of a compound of the formula (I)

$$R^1-CH_2-\underset{\displaystyle OR^3}{\underset{|}{CH}}-CH_2-R^2 \qquad (I)$$

where R^1 and R^2 are identical or different and each is



, -O-α-naphthyl or -O-β-naphthyl, where R^4, R^5 and R^6 are identical or different

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and each is H, C_1-C_{12} -alkyl or C_7-C_{10}- aralkyl, R^3 is a radical of the formula (II) or (III)

$$-(C_2H_4O)_n(C_3H_6O)_mH \quad \text{(II)}$$

$$-(C_3H_6O)_m(C_2H_4O)_nH, \quad \text{(III)}$$

where n is a number from 0 to 50 and m is a number from 0 to 50, with the proviso that m or n is 5 or more, and R^7 is hydrogen, 3) a suitable solvent for said agent and 4) water.

9. The crop protection oil-in-water emulsion of claim 8 wherein an anionic surfactant is used in addition to the nonionic emulsifier.

10. The crop protection oil-in-water emulsion of claim 9 wherein the anionic surfactant is a calcium salt of a mono- or dialkylbenzene sulfonate.

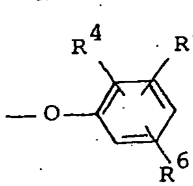
11. The crop protection oil-in-water emulsion of claim 10 wherein the weight ratio of nonionic surfactant to anionic surfactant is from 75:25 to 30:70.

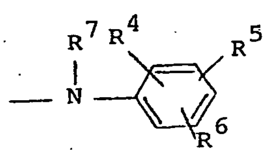
12. The crop protection oil-in-water emulsion of claim 11 which contains xylene or toluene as a solvent.

13. A crop protection composition comprising a crop protecting agent and as a nonionic oil-in-water emulsifier an effective amount of a compound of the formula (I)

$$R^1\text{-}CH_2\text{-}\underset{\displaystyle OR^3}{\underset{|}{CH}}\text{-}CH_2\text{-}R^2 \qquad \text{(I)}$$

where R^1 and R^2 are identical or different and each is





, -O-α-naphthyl or

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-O-β-naphthyl, where R^4, R^5 and R^6 are identical or different and each is H, C_1-C_{12} -alkyl or C_7-C_{10} - aralkyl, R^3 is a radical of the formula (II) or (III)

$$-(C_2H_4O)_n(C_3H_6O)_mH \qquad (II)$$

$$-(C_3H_6O)_m(C_2H_4O)_nH, \qquad (III)$$

where n is a number from 0 to 50 and m is a number from 0 to 50, with the proviso that m or n is 5 or more, and R^7 is hydrogen , said composition, if desired, including either a suitable solvent for said agent or water and a suitable solvent for said agent.